Title: Surface Ocean $^{13}C/^{12}C$ Measurements: a tracer of anthropogenic CO_2 uptake (through NOAA cooperative agreement #NA17RJ1232)

Duration: May 2004 to May 2007
Progress Report Period: May 2004 to Mar 2005

PI: Paul Quay

Institution: University of Washington

Introduction

About 40% of the CO_2 produced by human activities stays in the atmosphere with the remaining 60% accumulating in the ocean and terrestrial biota. The future rate of CO_2 build up in the atmosphere will depend on the rate of fossil fuel (and biomass) combustion and the CO_2 uptake rate by the oceans and terrestrial biota. Since global carbon cycle models will be used to predict future atmospheric CO_2 levels, it is important to improve the accuracy of these model predictions. Because the $^{13}C/^{12}C$ of CO_2 produced by combustion of fossil fuels and biomass is significantly lower than the $^{13}C/^{12}C$ of atmospheric CO_2, $^{13}C/^{12}C$ is a very useful tracer of the fate of anthropogenic CO_2. The observed decrease rate of $^{13}C/^{12}C$ of CO_2 in the atmosphere depends on the rate of anthropogenic CO_2 accumulation. Similarly, the observed decrease rate of $^{13}C/^{12}C$ of the dissolved inorganic carbon (DIC) in the ocean depends on the rate of anthropogenic CO_2 uptake by the ocean. Typically, the $^{13}C/^{12}C$ is expressed using the $\delta^{13}C$ notation where $\delta^{13}C$ (‰) = $[(^{13}C/^{12}C)\text{sample} / (^{13}C/^{12}C)\text{standard} – 1) * 1000$ and the standard is PDB.

We have estimated the rate of $^{13}C/^{12}C$ decrease in the ocean based on $^{13}C/^{12}C$ measurements during the WOCE program in the 1990s (Quay et al., 2003). The estimated ocean-wide $^{13}C/^{12}C$ decrease indicate that about 2 Gt C yr^{-1} are accumulating in the ocean compared to the ~8 Gt C yr^{-1} added to the atmosphere by human activity. We have observed that the largest $^{13}C/^{12}C$ decrease occurs in the subtropical oceans (15-40°) and the smallest decrease occurs at high latitudes. These regional patterns of $^{13}C/^{12}C$ decrease, generally, correlate well with the patterns of CO_2 (i.e., DIC) increase in the ocean. That is, anthropogenic CO_2 is accumulating at the fastest rate in the subtropical oceans and at the slowest rate in the Southern Ocean. This difference in regional CO_2 accumulation rates is likely a result of the large-scale circulation of the ocean.

Project Goals

Measure the change in the $^{13}C/^{12}C$ of DIC in the surface ocean in order to determine the rate of oceanic uptake of anthropogenic CO_2 using, first, atmospheric CO_2 and $^{13}CO_2$ budgets and, second, ocean models of CO_2 and $^{13}CO_2$ uptake.

Methods to Estimate Oceanic CO_2 Uptake Rate

Atmospheric CO_2 and $^{13}CO_2$ Budgets – Two atmospheric CO_2 budgets, one for $^{12}CO_2$ and one for $^{13}CO_2$, can be constructed. The CO_2 input is from fossil fuel combustion and biomass burning. The outputs are CO_2 uptake by the ocean and land biota. Since we know the rate of anthropogenic CO_2 addition to the atmosphere (~8 Gt/yr) and the $\delta^{13}C$ of this added CO_2 (~-28 ‰) and the rate of CO_2 increase (from 280 ppm to 380 ppm over the industrial era) and $\delta^{13}C$ decrease (from –6.4 ‰ to –8 ‰ over the industrial era) in the atmosphere has been measured, we can use the $^{12}CO_2$ and $^{13}CO_2$ budgets to solve for two CO_2 fluxes, that is, the net uptake rates of CO_2 by the ocean and terrestrial biota. Fortunately, the $\delta^{13}C$ of the CO_2 adsorbed by the ocean differs from the $\delta^{13}C$ of the CO_2 taken up via photosynthesis by the terrestrial biota. In order to solve these budgets for CO_2 uptake by the land biota and ocean, we need to estimate the $\delta^{13}C$ of the surface ocean (and CO_2 respired by land biota). Thus an immediate goal of our work is measure the $\delta^{13}C$ of the surface ocean with enough temporal and spatial resolution to accurate determine the latitudinal trends in the $\delta^{13}C$ for each ocean basin.

Modeling the Oceanic Uptake Rate of CO_2- The rate of $\delta^{13}C$ decrease in the surface ocean depends on the rate of anthropogenic CO_2 uptake. Ocean models predict that the greater the depth-integrated increase in anthropogenic CO_2 burden, the lower the surface $\delta^{13}C$ decrease and vice versa (Bacastow et al, 1996; Heimann and Maier-Reimer, 1996; Quay et al., 2003). This inverse relationship can be explained by considering that the deeper the layer of the ocean that can take up CO_2 the smaller the per volume change in $\delta^{13}C$, but the larger depth-integrated uptake. Thus by measuring the rate of $\delta^{13}C$ decrease in the surface ocean, one can estimate the CO_2 uptake rate.
The observed $\delta^{13}C$ decrease rate in the surface ocean varies with latitude due to the combination of the long (10 year) air-sea isotopic equilibration time and the varying residence time of surface waters. We find that the surface ocean $\delta^{13}C$ decrease rate in the subtropical gyres approaches the observed atmospheric $\delta^{13}C$ decrease rate (currently ~0.3 ‰ per decade), whereas the $\delta^{13}C$ change in the Southern Ocean is <0.1 ‰ per decade (McNeil et al., 2001, Quay and Stutsman, 2003). Thus measurements of the latitudinal trend in the $\delta^{13}C$ decrease of the surface ocean will provide useful constraints for ocean models used to estimate CO_2 uptake rates.

Results and Accomplishments

Sample Collection – Our approach to obtain the greatest spatial and temporal coverage of the $\delta^{13}C$ change in the surface ocean is to use Volunteer Observing Ships (VOSs) for sample collection. Seawater samples for the analysis of the $^{13}C/^{12}C$ of the DIC can be collected while underway using the ship's seawater intake line. These samples can be preserved for several years if the sample is poisoned and sealed against air. In the first year of this grant, we have initiated $\delta^{13}C$-DIC sample collections on several ships including the *Polar Sea* Coast Guard ice breaker between Seattle and McMurdo, Antarctica, the *Polarstern* a German research vessel between Bremen, Germany and Cape Town, S. Africa, *Waikato Columbus* a container ship between Seattle and Auckland, NZ, the *Atlantic Meridional Transect* (AMT) cruises between England and S. Africa, the *FICARAM* cruises between Spain and Argentina, the *L.M. Gould* cruises between Punta Aranus and Antarctica, the *Astrolabe* cruises between Tasmania and Antarctica. There are a few other VOSs that we intend to incorporate into this sampling network. We have collected a total of ~850 samples for $\delta^{13}C$ analysis on these cruises over the last year.

$\delta^{13}C$ Measurements- To date we have measured the $\delta^{13}C$-DIC on ~550 samples collected on these VOSs. The most noticeable outcome of the $\delta^{13}C$-DIC samples measured to date, has been the significant $\delta^{13}C$ decrease in the surface waters of the North Atlantic Ocean over the last decade. A comparison of the $\delta^{13}C$ measurement made during the A16N cruise (65ºN to 5ºS along 25ºW) during July 2003 in the N. Atlantic with a cruise (NOAA RITS93) along the same cruise track in July 1993, indicates that the $\delta^{13}C$ of the surface waters have decreased substantially especially in the subpolar waters north of 40ºN (Fig. 1). The surface ocean $\delta^{13}C$ decrease north of 40ºN is >0.4 ‰ over the decade interval between cruises, exceeding the atmospheric $\delta^{13}C$ decrease is ~0.3 ‰ over this interval. Furthermore, the surface ocean $\delta^{13}C$ decrease is significantly correlated with increase in phosphate and salinity in the subpolar latitudes. Thus a portion of this subpolar $\delta^{13}C$ decrease is likely due to changes in ventilation and/or photosynthesis and respiration rates. These results were presented at the Fall AGU (Quay and Stutsman, 2004).

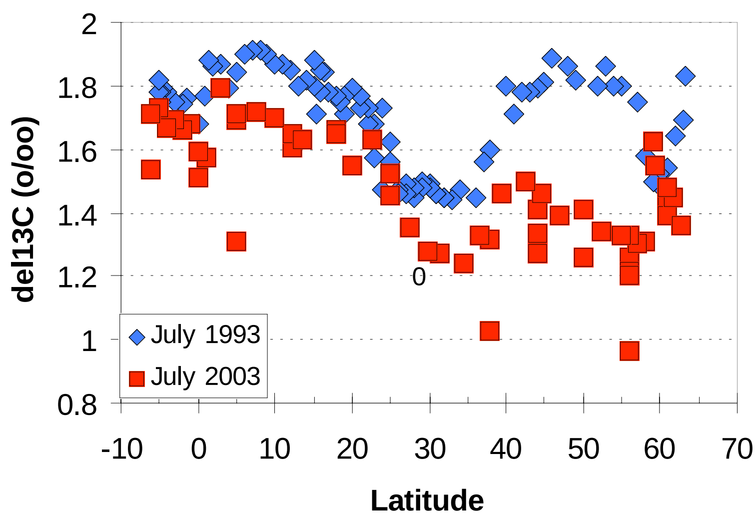

Fig. 1 The $\delta^{13}C$ of DIC measured in the surface waters of the N. Atlantic along 25ºW during a NOAA RITS cruise in 1993 and the Repeat Hydrography A16N cruise in 2003.

References

Bacastow, R.B., C.D. Keeling, T.J. Lueker, M. Wahlen, and W.G. Mook, The $\delta^{13}C$ Suess effect in the world surface oceans and its implications for oceanic uptake of CO_2: Analysis of observations at Bermuda, *Global Biogeochem. Cycles*, *10*, 335-346, 1996.

Heimann, M., and E. Maier-Reimer, On the relations between the oceanic uptake of CO_2 and its carbon isotopes, *Global Biogeochem. Cycles*, *10*, 89-110, 1996.

McNeil, B. I., R. J. Matear and B. Tilbrook (2001) Does carbon 13 track anthropogenic CO_2 in the Southern Ocean? *Global Biogeochemical Cycles*, **15**, 3, 597-613.
Quay, P. D., R. E. Sonnerup, T. Westby, J. Stutsman and A. P. McNichol (2003) Anthropogenic changes of the $^{13}C/^{12}C$ of dissolved inorganic carbon in the ocean as a tracer of CO_2 uptake, *Global Biogeochemical Cycles*, 17: January 2003 issue.
Quay, P.D. and J. Stutsman, Changes in the $^{13}C/^{12}C$ of dissolved inorganic carbon in the N. Atlantic along A16N between 1993 and 2003, EOS Fall AGU (2004).

Contacts

PI: Paul Quay (206-685-8061 (-3351 FAX), pdquay@u.washington.edu)

School of Oceanography
Box 355351
University of Washington
Seattle, WA 98195

Web Links: http://www.ocean.washington.edu/research/sil/index.html